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(54) METHOD FOR FORMING PLASMA FILMS

(57) In a case where a CF film is used as an inter-layer dielectric film for a semiconductor device, when a wiring of W (tungsten) is formed, the CF film is heated to a temperature of, e.g., about 400 to 450°C. At this time, F gases are desorbed from the CF film, so that there are various disadvantages due to the corrosion of the wiring and the decrease of film thickness.

As thin-film deposition gases, cyclic C₅F₈ gas and a hydrocarbon gas, e.g., C₂H₄ gas, are used. These gases are activated as plasma under a pressure of, e.g.,

0.1 Torr, to deposit a CF film on a semiconductor wafer at a process temperature of 400°C using active species thereof.

Alternatively, cyclic C₆F₆ gas is used as a thin-film deposition gas, and activated as plasma under a pressure of, e.g., 0.06 Pa, to deposit a CF film on a semiconductor wafer at a process temperature of 400°C using active species thereof.

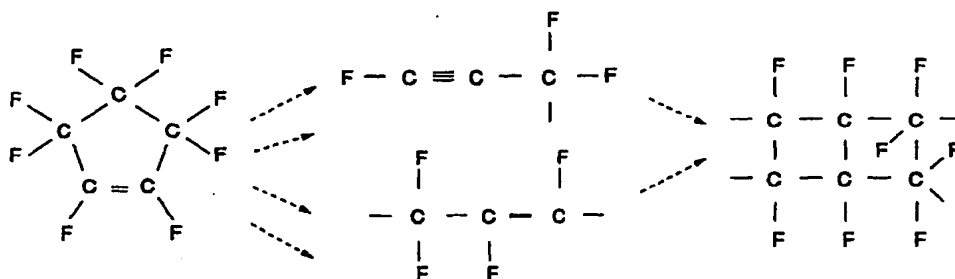


FIG.2

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Description

TECHNICAL FIELD

[0001] The present invention relates to a method for depositing a fluorine containing carbon film, which can be used as, e.g., an interlayer dielectric film (an interlayer dielectric film) of a semiconductor device, by a plasma treatment.

BACKGROUND ART

[0002] In order to achieve the high integration of a semiconductor device, it has been developed to provide devices, such as the scale down of a pattern and the multilayering of a circuit. As one of such devices, there is a technique for multilayering wirings. In order to provide a multi-layer metallization structure, a number n wiring layer and a number $(n+1)$ wiring layer are connected to each other by means of a conductive layer, and a thin-film called an interlayer dielectric film as an interlayer dielectric film is formed in a region other than the conductive layer.

[0003] A typical interlayer dielectric film is an SiO_2 film. In recent years, in order to more accelerate the operation of a device, it has been required to reduce the relative dielectric constant of the interlayer dielectric film, and the material of the interlayer dielectric film has been studied. That is, the relative dielectric constant of an SiO_2 film is about 4, and it has been diligently studied to dig up materials having a smaller relative dielectric constant than that of the SiO_2 film. As one of such materials, it has been studied to put an SiOF film having a relative dielectric constant of 3.5 to practical use. The inventor has taken notice of a fluorine containing carbon film (which will be hereinafter referred to as a "CF film") having a still smaller relative dielectric constant.

[0004] FIG. 19 shows a part of a circuit part formed on a wafer, wherein reference numbers 11 and 12 denote CF films, 13 and 14 denoting conductive layers of tungsten (W), 15 denoting a conductive layer of aluminum (Al), 16 denoting an SiO_2 film, into which P and B have been doped, and 17 denoting an n-type semiconductor region. The W layer 13 is formed at a process temperature of 400 to 450°C. At this time, the CF films 11 and 12 are heated to the process temperature. However, if the CF films are heated to such a high temperature, a part of C-F bonds are cut, so that F (fluorine) gases are mainly desorbed. The F gasses include F, CF, CF_2 gases and so forth.

[0005] If the F gases are thus desorbed, there are the following problems.

(a) The metal wirings of aluminum, tungsten and so forth are corroded.

(b) Although the insulator film also has the function of pressing the aluminum wiring to prevent the swell of aluminum, the pressing force of the insulator film

on the aluminum wiring is decreased by the degassing. As a result, the aluminum wiring swells, so that an electrical defect called electromigration is easily caused.

(c) The insulator film cracks, so that the insulation performance between the wirings gets worse. When the extent of the crack increases, it is not possible to form any wiring layers at the next stage.
(d) If the amount of desorbed F increases, the relative dielectric constant increases.

[0006] DISCLOSURE OF THE INVENTION

[0007] It is therefore an object of the present invention to eliminate the aforementioned problems and to provide a method capable of depositing an insulator film of a CF film, which has strong bonds and which is difficult to be decomposed, e.g., an interlayer dielectric film of a semiconductor device.

[0008] According to one aspect of the present invention, according to a first aspect of the present invention, a plasma thin-film deposition method comprises the steps of: activating a thin-film deposition gas containing cyclic C_5F_8 gas to form a plasma; and depositing an insulator film of a fluorine containing carbon film on a substrate to be treated, with the plasma.

[0009] The thin-film deposition gas may contain cyclic C_5F_8 gas and at least one of a hydrocarbon gas and hydrogen. The insulator film may be deposited under a process pressure of 5.5 Pa or lower. The temperature of the substrate to be treated may be 360°C or higher.

[0010] According to a second aspect of the present invention, a plasma thin-film deposition method comprises the steps of: activating a thin-film deposition gas containing linear C_5F_8 gas to form a plasma; and depositing an insulator film of a fluorine containing carbon film on a substrate to be treated, with the plasma.

[0011] The thin-film deposition gas may contain linear C_5F_8 gas and at least one of a hydrocarbon gas and hydrogen. The insulator film may be deposited under a process pressure of 0.3 Pa or lower. The temperature of the substrate to be treated may be 360°C or higher.

[0012] According to a third aspect of the present invention, a plasma thin-film deposition method comprises the steps of: activating a thin-film deposition gas containing a gas of a benzene ring containing compound to form a plasma; and depositing an insulator film of a fluorine containing carbon film on a substrate to be treated, with the plasma.

[0013] The benzene ring containing compound may be a compound of C and F. The compound of C and F may be C_6F_6 . The compound of C and F may also be C_7F_8 . Alternatively, the benzene ring containing compound may be a compound of C, F and H. The compound of C, F and H may be $\text{C}_7\text{H}_5\text{F}_3$.

[0014] According to the first through third aspects of the present invention, it is possible to produce a CF film

which has high thermostability and a small amount of desorbed F gas. Therefore, if this CF film is used as, e.g., an interlayer dielectric film of a semiconductor device, it is possible to prevent the corrosion of a metal wiring, the swell of an aluminum wiring and the crack of the film. Since CF films have been widely noticed as insulator films having a small relative dielectric constant and since the scale down and high integration of semiconductor devices have been required, the present invention is effective in the practical use of CF films as insulator films.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]

FIG. 1 is a longitudinal section of an example of a plasma treatment system for carrying out a method according to the present invention;
 FIG. 2 is a schematic diagram for explaining the decomposition and recombination of a thin-film deposition gas for use in the first preferred embodiment of the present invention;
 FIG. 3 is a characteristic diagram showing the results of a mass spectrometry when cyclic C_5F_8 gas is decomposed;
 FIG. 4 is a schematic diagram for explaining the decomposition and recombination of C_4F_8 gas compared with the thin-film deposition gas for use in the first preferred embodiment of the present invention;
 FIG. 5 is a schematic sectional view of a measuring device for examining the variation in weight of a thin-film;
 FIG. 6 is a characteristic diagram showing the relationship between the variations in weight of a CF film, which is deposited using cyclic C_5F_8 gas and C_2H_4 gas, and process temperatures;
 FIG. 7 is a characteristic diagram showing the relationship between the variations in weight of a CF film, which is deposited using cyclic C_5F_8 gas and C_2H_4 gas, and the flow ratios of thin-film deposition gases;
 FIG. 8 is a characteristic diagram showing the relationship between the variations in weight of a CF film, which is deposited using cyclic C_5F_8 gas and C_2H_4 gas, and process pressures;
 FIG. 9 is a characteristic diagram showing the relationship between the variations in weight of a CF film, which is deposited using cyclic C_5F_8 gas and C_2H_4 gas, and process temperatures;
 FIG. 10 is a characteristic diagram showing the relationship between the variations in weight of a CF film, which is deposited using cyclic C_5F_8 gas and C_2H_4 gas, and the flow ratios of thin-film deposition gases;
 FIG. 11 is a characteristic diagram showing the relationship between the variations in weight of a

CF film, which is deposited using cyclic C_5F_8 gas and C_2H_4 gas, and process pressures;

FIG. 12 is a characteristic diagram showing the relationship between the variations in weight of a CF film, which is deposited using linear C_5F_8 gas and C_2H_4 gas, and process temperatures;

FIG. 13 is a characteristic diagram showing the relationship between the variations in weight of a CF film, which is deposited using linear C_5F_8 gas and C_2H_4 gas, and the flow ratios of thin-film deposition gases;

FIG. 14 is a characteristic diagram showing the relationship between the variations in weight of a CF film, which is deposited using linear C_5F_8 gas and C_2H_4 gas, and process pressures;

FIG. 15 is a characteristic diagram showing the results of a mass spectrometry when linear C_5F_8 gas is decomposed;

FIG. 16 is a schematic diagram showing the variations in weight of CF films in Examples and Comparative Examples;

FIG. 17 is a characteristic diagram showing the results of a mass spectrometry when C_4F_8 gas is decomposed;

FIG. 18 is a characteristic diagram showing the results of a mass spectrometry for CF films at a high temperature;

FIG. 19 is a structural drawing showing an example of the structure of a semiconductor device;

FIG. 20 is a schematic diagram for explaining the decomposition and recombination of a thin-film deposition gas for use in the second preferred embodiment of the present invention;

FIG. 21 is a schematic diagram showing molecular formulae of examples of thin-film deposition gases;

FIG. 22 is a schematic diagram showing molecular formulae of examples of thin-film deposition gases;

FIG. 23 is a schematic diagram showing the variations in weight in Examples and Comparative Examples;

FIG. 24 is a characteristic diagram showing the results of a mass spectrometry for CF films at a high temperature in Example;

FIG. 25 is a characteristic diagram showing the results of a mass spectrometry for CF films at a high temperature in Comparative Example;

FIG. 26 is a characteristic diagram showing the results of a mass spectrometry when hexafluorobenzene is decomposed;

FIG. 27 is a characteristic diagram showing the results of a mass spectrometry when octafluorotoluene is decomposed; and

FIG. 28 is a characteristic diagram showing the results of a mass spectrometry when 1,4-bis(trifluoromethyl)benzene is decomposed.

BEST MODE FOR CARRYING OUT THE INVENTION

[0016] FIG. 1 shows an example of a plasma treatment system for use in the preferred embodiments of the present invention. This system has a vacuum vessel 2 of, e.g., aluminum. The vacuum vessel 2 comprises a first cylindrical vacuum chamber 21, which is arranged in an upper portion for producing a plasma, and a second cylindrical vacuum chamber 22, which is communicated with and connected to the lower portion of the first vacuum chamber 21 and which has a greater diameter than that of the first vacuum chamber 21. Furthermore, the vacuum vessel 2 is grounded to have a zero potential.

[0017] The upper end of the vacuum vessel 2 is open. A transmission window 23 of a microwave permeable material, e.g., quartz, is airtightly provided in the open upper end of the vacuum vessel 2 so as to hold vacuum in the vacuum vessel 2. Outside of the transmission window 23, there is provided a waveguide 25 connected to a high-frequency power supply part 24 for producing a microwave of, e.g., 2.45 GHz. The microwave produced by the high-frequency power supply part 24 is guided by the waveguide 25 in, e.g., a TE mode, or the microwave guided in the TE mode is converted by the waveguide 25 into a TM mode, to be introduced from the transmission window 23 into the first vacuum chamber 21.

[0018] In the side wall defining the first vacuum chamber 21, gas nozzles 31 are arranged at regular intervals along, e.g., the periphery thereof. The gas nozzles 31 are connected to a gas source (not shown), e.g., an Ar gas source, so that Ar gas can be uniformly supplied to the upper portion in the first vacuum chamber 21.

[0019] In the second vacuum chamber 22, a wafer mounting table 4 is provided so as to face the first vacuum chamber 21. The mounting table 4 has an electrostatic chuck 41 on the surface thereof. The electrode of the electrostatic chuck 41 is connected to a dc power supply (not shown) for absorbing a wafer and to a high-frequency power supply part 42 for applying a bias voltage for implanting ions into the wafer.

[0020] On the other hand, in the upper portion of the second vacuum chamber 22, i.e., an a portion of the second vacuum chamber 22 communicated with the first vacuum chamber 21, a ring-shaped thin-film deposition gas supply part 51 is provided. For example, two kinds of thin-film deposition gases are supplied from gas supply pipes 52 and 53 to the thin-film deposition gas supply part 51, so that the mixed gas thereof is supplied to the vacuum vessel 2 via gas holes 54 formed in the inner peripheral surface of the thin-film deposition gas supply part 51.

[0021] In the vicinity of the outer periphery of the side wall defining the first vacuum chamber 21, a magnetic field forming means, e.g., a ring-shaped main electromagnetic coil 26, is arranged. Below the second

vacuum chamber 22, a ring-shaped auxiliary electromagnetic coil 27 is arranged. To the bottom of the second vacuum chamber 22, exhaust pipes 28 are connected at, e.g., two positions which are symmetrical with respect to the central axis of the vacuum chamber 22.

[0022] The first preferred embodiment of the present invention will be described below.

[0023] A method for depositing an interlayer dielectric film of a CF film on a wafer W, which serves as a substrate to be treated, using the system shown in FIG. 1 will be described. First, a gate valve (not shown) provided in the side wall of the vacuum vessel 2 is open, and the wafer W, on which a wiring of, e.g., aluminum, has been formed, is introduced from a load-lock chamber (not shown) by means of a transport arm (not shown) to be mounted on the mounting table 4 to be electrostatically absorbed by means of the electrostatic chuck 41.

[0024] Subsequently, after the gate valve is closed to seal the interior of the vacuum vessel 2, the internal atmosphere is exhausted by the exhaust pipes 28, and the interior of the vacuum vessel 2 is evacuated to a predetermined degree of vacuum. Then, a plasma producing gas, e.g., Ar gas, is introduced from the plasma gas nozzles 31 into the first vacuum chamber 21 at a predetermined flow rate, and a thin-film deposition gas is introduced from the thin-film deposition gas supply part 5 into the second vacuum chamber 22 at a predetermined flow rate.

[0025] This preferred embodiment is characterized by the thin-film deposition gas. As shown on the left side of FIG. 2(a), cyclic C_5F_8 gas is used as the thin-film deposition gas. As the thin-film deposition gas, a hydrocarbon gas, e.g., C_2H_4 gas is also used. The C_5F_8 and C_2H_4 gasses are supplied to the vacuum vessel 2 via the thin-film deposition gas supply part 5 from the gas supply pipes 52 and 53, respectively. Then, the interior of the vacuum vessel 2 is held under a predetermined process pressure, and a bias voltage of 13.56 MHz and 1500 W is applied to the mounting table 4 by means of the high-frequency power supply part 42. In addition, the surface temperature of the mounting table 4 is set to be about 400°C.

[0026] A high-frequency wave (a microwave) of 2.45 GHz from the high-frequency power supply part 24 passes through the waveguide 25 to reach the ceiling of the vacuum vessel 2, and passes through the transmission window 23 to be introduced into the first vacuum chamber 21. On the other hand, a magnetic field extending from the upper portion of the first vacuum chamber 21 to the lower portion of the second vacuum chamber 22 is formed in the vacuum vessel 2 by the electromagnetic coils 26 and 27. The intensity of the magnetic field is, e.g., 875 gauss in the vicinity of the lower portion of the first vacuum chamber 21. The electron cyclotron resonance is produced by the interaction between the magnetic field and the microwave. By this

resonance, Ar gas is activated as plasma and enriched. The plasma flows from the first vacuum chamber 21 into the second vacuum chamber 22 to activate C_5F_8 gas and C_2H_4 gas, which have been supplied thereto, to form active species to deposit a CF film on the wafer W. Furthermore, when a device is actually produced, the CF film is etched with a predetermined pattern, and, e.g., a W film is embedded in a groove portion to form a W wiring.

[0027] The CF film thus deposited has a strong bond, and high thermostability as can be seen from the results of experiment which will be described later. That is, the amount of the desorbed F gases is small even at a high temperature. It is considered that the reason for this is that the decomposition products of cyclic C_5F_8 are easy to form a three-dimensional structure shown in FIG. 2, so that C-F bonds are strengthened and difficult to be cut even if heat is applied thereto. The decomposition products of cyclic C_5F_8 were vaporized under a reduced pressure of 0.002 Pa, and the vaporized decomposition products were analyzed by means of a mass spectrometer. The obtained results are shown in FIG. 3. It can be seen from the results that many C_3F_3 and C_4F_4 , which are easy to form three-dimensional structures, exist as decomposition products.

[0028] As a comparative example, considering a case where cyclic C_4F_8 gas is used as a thin-film deposition gas, the decomposition products of C_4F_8 include the most C_2F_4 to easily form a straight chain structure as shown in FIG. 4. Therefore, the thermostability of a CF film deposited using C_4F_8 gas is low, as can be seen from the results of comparative experiments which will be described later.

[0029] In view of the foregoing, C_5F_8 gas is essentially used as a thin-film deposition gas according to the present invention. As a gas added thereto, a hydrocarbon gas, such as C_2H_4 , CH_4 or C_2H_6 gas, hydrogen gas or a mixed gas of the hydrocarbon gas and hydrogen gas may be used.

(Example 1)

[0030] Using a measuring device shown in FIG. 5, the variation in weight of a thin-film at a high temperature was examined as an index of the thermostability of the thin-film. In FIG. 5, reference number 61 denotes a vacuum vessel, 62 denoting a heater, 63 denoting a crucible suspended from a beam of a light balance mechanism, and 64 denoting a weight measuring part. As a measuring method, there was adopted a method for shaving a CF film on a wafer to put the shaven CF film in the crucible 63 to raise the temperature in the crucible 63 to 425°C under a vacuum atmosphere to heat the CF film for 2 hours to examine the variation in weight in the weight measuring part 64. In the thin-film deposition process described above in the preferred embodiment, the temperature during the thin-film deposition was set to be any one of seven temperatures, 300°C, 325°C,

350°C, 360°C, 380°C, 400°C, 420°C and 440°C, and the variations in weight of CF films obtained at the respective process temperatures were examined. The results thus obtained are shown in FIG. 6.

[0031] In the above thin-film deposition process, the flow rates of C_5F_8 , C_2H_4 and Ar gases were set to be 60 sccm, 20 sccm and 150 sccm, respectively. In addition, the microwave power (the high-frequency power supply part 24) and the bias power (the high-frequency power supply part 42) were set to be 2000 W and 1500 W, respectively. Moreover, the process pressure was set to be 0.1 Pa. Furthermore, the variation in weight means a value of $\{(A-B)/A\} \times 100$ assuming that the weight of the thin-film in the crucible before heating is A and the weight of the thin-film in the crucible after heating is B.

[0032] As can be seen from FIG. 6, the variation in weight at a process temperature of 360°C is 2.8 % which is less than 3 %, and the variation in weight at a process temperature of 400°C or higher is 1.4 % which is very low, so that thermostability is high and the amount of degassing is small.

[0033] In addition, CF films were deposited at a process temperature of 400°C at various flow ratios of C_5F_8 gas to C_2H_4 gas when other process conditions were the same as the above described conditions. The variations in weight of the obtained CF films were examined. The results thus obtained are shown in FIG. 7. Furthermore, the flow ratio means C_5F_8/C_2H_4 , and the flow rate of C_5F_8 was fixed to 60 sccm. As can be seen from the results, the variation in weight is small, 1.4 %, when the flow ratio is 3. As the flow ratio decreases, the variation in weight decreases substantially in proportion thereto. When the flow ratio is less than 1, it is difficult to deposit a thin-film due to film peeling.

[0034] Moreover, CF films were deposited at a process temperature of 400°C under various process pressures when the flow rates of C_5F_8 gas and C_2H_4 gas were set to be 60 sccm and 20 sccm, respectively, and when other process conditions were the same as the above described conditions. The variations in weight of the obtained CF films were examined. The results thus obtained are shown in FIG. 8. As can be seen from the results, the variation in weight is small, 2 % or less, when the process pressure is lower than or equal to 5.5 Pa.

(Example 2)

[0035] CF films were obtained on various process conditions using hydrogen gas (H_2 gas) in place of C_2H_4 gas in Example 1. The variations in weight of the obtained CF films were examined. First, the temperature during the thin-film deposition was set to be any one of five temperatures, 300°C, 350°C, 360°C, 400°C and 420°C, and the variations in weight of the CF films obtained at the respective process temperatures were examined. The results thus obtained are shown in FIG. 9.

[0036] In the above process, the flow rates of C_5F_8 , H_2 and Ar gases were set to be 60 sccm, 40 sccm and 150 sccm, respectively. In addition, the microwave power (the high-frequency power supply part 24) and the bias power (the high-frequency power supply part 42) were set to be 2000 W and 1500 W, respectively. Moreover, the process pressure was set to be 0.2 Pa.

[0037] As can be seen from FIG. 9, the temperature dependency was substantially the same as that in Example 1. The variation in weight at a process temperature of 360°C is 2.8 % which is less than 3 %, and the variation in weight at a process temperature of 400°C or higher is 1.5 % which is very low, so that thermostability is high and the amount of degassing is small. Furthermore, no thin-film was deposited due to film peeling at a temperature of higher than 420°C.

[0038] In addition, CF films were deposited at a process temperature of 400°C at various flow ratios of C_5F_8 gas to H_2 gas when other process conditions were the same as the above described conditions. The variations in weight of the obtained CF films were examined. The results thus obtained are shown in FIG. 10. Furthermore, the flow ratio means C_5F_8/H_2 , and the flow rate of C_5F_8 was fixed to 60 sccm. When the flow rate was less than 0.8, no thin-film was deposited. On the other hand, even if the flow rate exceeded 2, no thin-film was deposited. In this range, the variation in weight was small, 2 % or less.

[0039] Moreover, CF films were deposited at a process temperature of 400°C under various process pressures when the flow rates of C_5F_8 gas and H_2 gas were set to be 60 sccm and 40 sccm, respectively, and when other process conditions were the same as the above described conditions. The variations in weight of the obtained CF films were examined. The results thus obtained are shown in FIG. 11. As can be seen from the results, the pressure dependency is substantially the same as that in Example 1, and the variation in weight is small, 2 % or less, when the process pressure is lower than or equal to 5.5 Pa.

(Example 3)

[0040] CF films were obtained using linear C_5F_8 gas (which will be hereinafter referred to as $\langle C_5F_8 \text{ gas} \rangle$) in place of cyclic C_5F_8 gas as a thin-film deposition gas when the temperature during the thin-film deposition was set to be any one of seven temperatures, 300°C, 325°C, 350°C, 360°C, 400°C, 420°C and 440°C. The variations in weight of the CF films obtained at the respective process temperatures were examined. The results thus obtained are shown in FIG. 12.

[0041] In the above process, the flow rates of $\langle C_5F_8 \text{ gas} \rangle$, C_2H_4 gas and Ar gas were set to be 60 sccm, 20 sccm and 150 sccm, respectively. In addition, the microwave power (the high-frequency power supply part 24) and the bias power (the high-frequency power supply part 42) were set to be 2000 W and 1500 w, respec-

tively. Moreover, the process pressure was set to be 0.1 Pa.

[0042] As can be seen from FIG. 12, the temperature dependency was substantially the same as that in Example 1. The variation in temperature at a process temperature of 360°C is 2.8 %, and the variation in temperature is substantially constant even if the process temperature rises. In the case of $\langle C_5F_8 \text{ gas} \rangle$, the variation in weight of the CF film exceeds 2 % which is greater than that in the case of cyclic C_5F_8 gas used in Example 1, although $\langle C_5F_8 \text{ gas} \rangle$ has the same molecular formula as that of cyclic C_5F_8 gas. It is considered that the reason for this is that cyclic C_5F_8 gas more easily form a three-dimensional structure. However, the variation in weight is less than 3 %, and thermostability is higher than that of C_4F_8 gas which will be described later, so that $\langle C_5F_8 \text{ gas} \rangle$ is effectively used as a thin-film deposition gas.

[0043] In addition, CF films were deposited at a process temperature of 400°C at various flow ratios of $\langle C_5F_8 \text{ gas} \rangle$ to C_2H_4 gas when other process conditions were the same as the above described conditions. The variations in weight of the obtained CF films were examined. The results thus obtained are shown in FIG. 13. Furthermore, the flow ratio means $\langle C_5F_8 \rangle / C_2H_4$, and the flow rate of $\langle C_5F_8 \text{ gas} \rangle$ was fixed to 60 sccm. When the flow rate was less than 1, it was difficult to maintain the deposited thin-film due to film peeling.

[0044] Moreover, CF films were deposited at a process temperature of 400°C under various process pressures when the flow rates of $\langle C_5F_8 \text{ gas} \rangle$ and C_2H_4 gas were set to be 60 sccm and 20 sccm, respectively, and when other process conditions were the same as the above described conditions. The variations in weight of the obtained CF films were examined. The results thus obtained are shown in FIG. 14. As can be seen from the results, the pressure dependency is different from that in Example 1, and the variation in weight is not 3 % or less unless the process pressure is 0.3 Pa or less. FIG. 15 shows the results of the mass spectrometry for $\langle C_5F_8 \text{ gas} \rangle$. It is guessed from these decomposition products that the CF film has a three-dimensional network structure.

(Comparative Example)

[0045] CF films were obtained using cyclic C_4F_8 gas in place of cyclic C_5F_8 gas as a thin-film deposition gas. The variations in weight of the obtained CF films were examined. The variation in weight was very large, 3.7 %. In this process, the flow rates of C_4F_8 and C_2H_4 gases were set to be 40 sccm and 30 sccm, respectively, and the process pressure was set to be 0.1 Pa. In addition, the microwave power was set to be 2700 W, and other conditions were the same as those in Example 1.

[0046] FIG. 16 shows the variation in weight of the thin-films deposited at a process temperature of 400°C

in Examples 1 and 3 and Comparative Example. As can be seen from these results, the variation in weight in the case of C_4F_8 gas is greater than that in the case of C_5F_8 gas or (C_5F_8 gas). It is guessed that the reason for this is that the CF film obtained by causing C_4F_8 gas to be decomposed and recombined as shown in FIG. 4 has many straight chain structures to have weak C-F bonds, so that the amounts of desorbed F, CF and CF_2 are large when heat is applied thereto. Furthermore, FIG. 17 shows the results of the mass spectrometry for C_4F_8 gas. As described above, it can be seen that many C_2F_4 exist as decomposition results.

[0047] In addition, the mass spectrometry was carried out at a high temperature with respect to the CF films obtained at a process temperature of 400 °C using cyclic C_5F_8 gas and C_4F_8 gas, respectively. Specifically, this measurement was carried out by a mass spectrometer connected to a vacuum vessel, in which a predetermined amount of thin-film was put and the interior of which was heated to 425°C. The results are shown in FIGS. 18(a) and 18(b). In these drawings, the axis of ordinates denotes a dimensionless amount corresponding to the intensity of spectrum, and the peaks thereof denote the desorption of the respective gases. In addition, the axis of abscissas denotes time after the temperature rise in the vacuum vessel begins. The temperature rises at a rate of 10°C/min from room temperature. After the temperature reaches 425°C, it is held for 30 minutes.

[0048] The amounts of F and HF desorbed from the CF films according to the present invention shown in FIG. 8(a) are far smaller than those in Comparative Example shown in FIG. 8(b). The amounts of CF, CF_2 and CF_3 shown in FIG. 8(a) are also smaller than those in FIG. 8(b). It can be also seen from the results of the mass spectrometry that the CF films deposited using cyclic C_5F_8 gas have strong bonds and high stability.

[0049] Moreover, according to the present invention, the plasma producing method should not be limited to the ECR, the plasma may be produced by, e.g., a method called ICP (Inductive Coupled Plasma) for applying electric and magnetic fields to a process gas from a coil wound onto a dome-shaped container.

[0050] The second preferred embodiment of the present invention will be described below.

[0051] A method for depositing an interlayer dielectric film of a CF film on a wafer W, which is a substrate to be treated, using the system shown in FIG. 1 will be described. First, a gate valve (not shown) provided in the side wall of the vacuum vessel 2 is open, and the wafer W, on which, e.g., an aluminum wiring has been formed, is introduced from a load-lock chamber (not shown) by means of a transport arm (not shown) to be put on the mounting table 4 to be electrostatically absorbed by means of the electrostatic chuck 41.

[0052] Subsequently, after the gate valve is closed to seal the interior of the vacuum vessel 2, the internal atmosphere is exhausted by the exhaust pipes 28, and

the interior of the vacuum vessel 2 is evacuated to a predetermined degree of vacuum. Then, a plasma producing gas, e.g., Ar gas, is introduced from the plasma gas nozzles 31 into the first vacuum chamber 21 at a predetermined flow rate, and a thin-film deposition gas is introduced from the thin-film deposition gas supply part 5 into the second vacuum chamber 22 at a predetermined flow rate.

[0053] This preferred embodiment is characterized by the thin-film deposition gas. As the thin-film deposition gas, a gas of a compound having a benzene ring (an aromatic compound), e.g., C_6F_6 (hexafluorobenzene), is used. Furthermore, when one kind of C_6F_6 is used as the thin-film deposition gas, it is supplied from one of the gas supply pipes 52 and 53 into the vacuum vessel 2 via the thin-film deposition gas supply part 51. Then, the interior of the vacuum vessel 2 is held at a predetermined process pressure, and a bias voltage of, e.g., 13.56 MHz and 1500 W, is applied to the mounting table 4 by means of the high-frequency power supply part 42. In addition, the surface temperature of the mounting table 4 is set to be about 400°C.

[0054] A high-frequency wave (a microwave) of 2.45 GHz from the high-frequency power supply part 24 passes through the waveguide 25 to reach the ceiling of the vacuum vessel 2, and passes through the transmission window 23 to be introduced into the first vacuum chamber 21. On the other hand, a magnetic field extending from the upper portion of the first vacuum chamber 21 to the lower portion of the second vacuum chamber 22 is formed in the vacuum vessel 2 by the electromagnetic coils 26 and 27. The intensity of the magnetic field is, e.g., 875 gauss, in the vicinity of the lower portion of the first vacuum chamber 21. The electron cyclotron resonance is produced by the interaction between the magnetic field and the microwave. By this resonance, Ar gas is activated as plasma and enriched. The plasma flows from the first vacuum chamber 21 into the second vacuum chamber 22 to activate C_6F_6 , which have been supplied thereto, to form active species to deposit a CF film on the wafer W. Furthermore, when a device is actually produced, the CF film is etched with a predetermined pattern, and, e.g., a W film is embedded in a groove portion to form a W wiring.

[0055] The CF film thus deposited has a strong bond, and high thermostability as can be seen from the results of experiment which will be described later. The reason for this is that benzene ring is stable since it resonates between states A and B so that each of C-C bonds is in the intermediate state between a single bond and a double bond as shown in FIG. 20. Therefore, it is considered that the C-C bonds of the benzene ring existing in the CF film, and the bonds between C of the benzene ring and C outside the benzene ring have strong bonding force, so that the amounts of the desorbed CF, CF_2 and CF_3 are small.

[0056] FIGS. 21 and 22 show examples of benzene ring containing compounds for use in the present inven-

tion.

(Example 1)

[0057] Using a measuring device shown in FIG. 5, the variation in weight of a thin-film at a high temperature was examined as an index of the thermostability of the thin-film. In FIG. 5, reference number 61 denotes a vacuum vessel, 62 denoting a heater, 63 denoting a crucible suspended from a beam of a light balance mechanism, and 64 denoting a weight measuring part. As a measuring method, there was adopted a method for shaving a CF film on a wafer to put the shaven CF film in the crucible 63 to raise the temperature in the crucible 63 to 425°C under a vacuum atmosphere to heat the CF film for 2 hours to examine the variation in weight in the weight measuring part 64. In the thin-film deposition process described above in the preferred embodiment, the flow rates of C₆F₈ (hexafluorobenzene) gas and Ar gases were set to be 40 sccm and 30 sccm, respectively. In addition, the temperature of the wafer W was set to be 400°C, and the process pressure was set to be 0.06 Pa. Moreover, the microwave power (the power of the high-frequency power supply part 24) and the bias power (the power of the high-frequency power supply part 42) were set to be various values. The variations in weight of the CF films obtained on the respective conditions were examined. Furthermore, the variation in weight means a value of $\{(A-B)/A\} \times 100$ assuming that the weight of the thin-film in the crucible before heating is A and the weight of the thin-film in the crucible after heating is B.

[0058] Moreover, the mass spectrometry was carried out at a high temperature with respect to the CF films obtained at a microwave power of 1.0 kW at a bias power of 1.5 kW on the aforementioned process conditions. Specifically, this measurement was carried out by a mass spectrometer connected to a vacuum vessel, in which a predetermined amount of thin-film was put and the interior of which was heated to 425°C. The results are shown in FIGS. 24. In this drawing, the axis of ordinates denotes a dimensionless amount corresponding to the intensity of spectrum, and the peaks thereof denote the desorption of the respective gases. In addition, the axis of abscissas denotes time after the temperature rise in the vacuum vessel begins. The temperature rises at a rate of 10°C/min from room temperature. After the temperature reaches 425°C, it is held for 30 minutes.

(Example 2)

[0059] A CF film was deposited on the wafer on the same conditions as those in Example 1, except that C₇F₈ (octafluorotoluene) gas was substituted for C₆F₆ gas, the flow rates of C₇F₈ gas and Ar gas were set to be 40 sccm and 40 sccm, respectively, the process pressure was 0.07 Pa, the microwave power was set to

be 1.0 kW and the bias power was set to be 1.0 kW. With respect to this CF film, the variation in weight was examined in the same manner as that in Example 1. The variation in weight was 1.9 % (see FIG. 23).

(Example 3)

[0060] A CF film was deposited on the wafer on the same conditions as those in Example 1, except that C₄F₈ gas and C₇H₅F₃ (trifluoromethylbenzene) gas were substituted for C₆F₆ gas, the flow rates of C₄F₈ gas, C₇H₅F₃ gas and Ar gas were set to be 20 sccm, 20 sccm and 30 sccm, respectively, the process pressure was 0.07 Pa, the microwave power was set to be 1.0 kW and the bias power was set to be 1.0 kW. With respect to this CF film, the variation in weight was examined in the same manner as that in Example 1. The variation in weight was 2.0 % (see FIG. 23).

(Comparative Example)

[0061] A CF film was deposited on the wafer on the same conditions as those in Example 1, except that C₄F₈ gas and C₂H₄ gas were substituted for C₆F₆ gas, the flow rates of C₄F₈, C₂H₄ gas and Ar gas were set to be 40 sccm, 30 sccm and 150 sccm, respectively, the process pressure was set to be 0.22 Pa, the microwave power was set to be 2.0 kW and the bias power was set to be 1.5 kW. With respect to this CF film, the variation in weight was examined in the same manner as that in Example 1. The variation in weight was 4.4 % (see FIG. 23).

[0062] Moreover, with respect to this CF film, the mass spectrometry was carried out in the same manner as that in Example 1. The results thereof are shown in FIG. 25.

(Consideration)

[0063] As can be seen from Examples 1 and 2, when C₆F₆ gas or C₇F₈ gas is used, the variation in weight is a level of 1 %, so that thermostability is high and the amount of degassing is small. In particular, when C₆F₆ gas is used, thermostability is very high. As can be seen from the comparison of FIG. 24 with FIG. 25, when C₆F₆ gas is used, the amounts of the desorbed CF, CF₂ and CF₃ are smaller than those when C₄F₈ gas and C₂H₄ gas are used. This meets the guess that C-C bonds are difficult to be cut when a material gas of an aromatic compound is used as described above. It is considered that the decomposition products of C₆F₆ gas are C₆F₆, C₅F₃, C₃F₃ and so forth which have double bonds. The recombination product thereof has a three-dimensional structure and strong bonds. Even at a high temperature, the bonds of the recombination product are difficult to be cut, so that the amount of degassing is small.

[0064] It is guessed that the reason why the varia-

tions in weight in Examples 3 and 4 is a level of 2 %, which is greater than those in Examples 1 and 2 although it is less than that in Comparative Example, is as follows. That is, if C_7F_8 gas or $C_7H_5F_3$ gas is used alone, F is insufficient, so that C_4F_8 gas is added. The network structure is reduced by the thin-film deposited on the basis of the decomposition products of C_7F_8 gas, so that the C-C bonds are cut to be desorbed as CF, CF_2 and CF_3 . As a result, the variation in weight is greater than that when C_6F_6 gas or C_7F_8 gas is used.

[0065] The decomposition products of C_6F_6 , C_7F_8 and $C_8H_4F_6$ (1, 4-bistrifluoromethylbenzene) are vaporized under a reduced pressure of 0.002 Pa, and the vaporized decomposition products were analyzed by means of a mass spectrometer. The obtained results are shown in FIGS. 26 through 28. It can be seen from these results that many benzene ring containing components exist as decomposition products, so that it can be guessed that a stable CF film having a network structure is produced.

[0066] Moreover, according to the present invention, the plasm producing method should not be limited to the ECR, the plasma may be produced by, e.g., a method called ICP (Inductive Coupled Plasma) for applying electric and magnetic fields to a process gas from a coil wound onto a dome-shaped container.

[0067] The first and second preferred embodiments of the present invention have been described above. According to these preferred embodiments, it is possible to produce a CF film which has high thermostability and a small amount of desorbed F gas. Therefore, if this CF film is used as, e.g., an interlayer dielectric film of a semiconductor device, it is possible to prevent the corrosion of a metal wiring, the swell of an aluminum wiring and the crack of the film. Since CF films have been widely noticed as insulator films having a small relative dielectric constant and since the scale down and high integration of semiconductor devices have been required, the present invention is effective in the practical use of CF films as insulator films.

Claims

1. A plasma thin-film deposition method comprising the steps of:
 - activating a thin-film deposition gas containing cyclic C_5F_8 gas to form a plasm; and
 - depositing an insulator film of a fluorine containing carbon film on a substrate to be treated, with said plasma.
2. A plasm thin-film deposition method as set forth in claim 1, wherein said thin-film deposition gas contains cyclic C_5F_8 gas and at lease one of a hydrocarbon gas and hydrogen.
3. A plasm thin-film deposition method as set forth in claim 1, wherein said insulator film is deposited under a process pressure of 5.5 Pa or lower.
4. A plasm thin-film deposition method as set forth in claim 1, wherein the temperature of said substrate to be treated is 360°C or higher.
5. A plasm thin-film deposition method comprising the steps of:
 - activating a thin-film deposition gas containing linear C_5F_8 gas to form a plasma; and
 - depositing an insulator film of a fluorine containing carbon film on a substrate to be treated, with said plasm.
6. A plasm thin-film deposition method as set forth in claim 5, wherein said thin-film deposition gas contains linear C_5F_8 gas and at lease one of a hydrocarbon gas and hydrogen.
7. A plasma thin-film deposition method as set forth in claim 5, wherein said insulator film is deposited under a process pressure of 0.3 Pa or lower.
8. A plasma thin-film deposition method as set forth in claim 5, wherein the temperature of said substrate to be treated is 360°C or higher.
9. A plasma thin-film deposition method comprising the steps of:
 - activating a thin-film deposition gas containing a gas of a benzene ring containing compound to form a plasma; and
 - depositing an insulator film of a fluorine containing carbon film on a substrate to be treated, with said plasm.
10. A plasma thin-film deposition method as set forth in claim 9, wherein said benzene ring containing compound is a compound of C and F.
11. A plasm thin-film deposition method as set forth in claim 10, wherein said compound of C and F is C_6F_6 .
12. A plasm thin-film deposition method as set forth in claim 10, wherein said compound of C and F is C_7F_8 .
13. A plasm thin-film deposition method as set forth in claim 9, wherein said benzene ring containing compound is a compound of C, F and H.
14. A plasm thin-film deposition method as set forth in claim 13, wherein said compound of C, F and H is $C_7H_5F_3$.

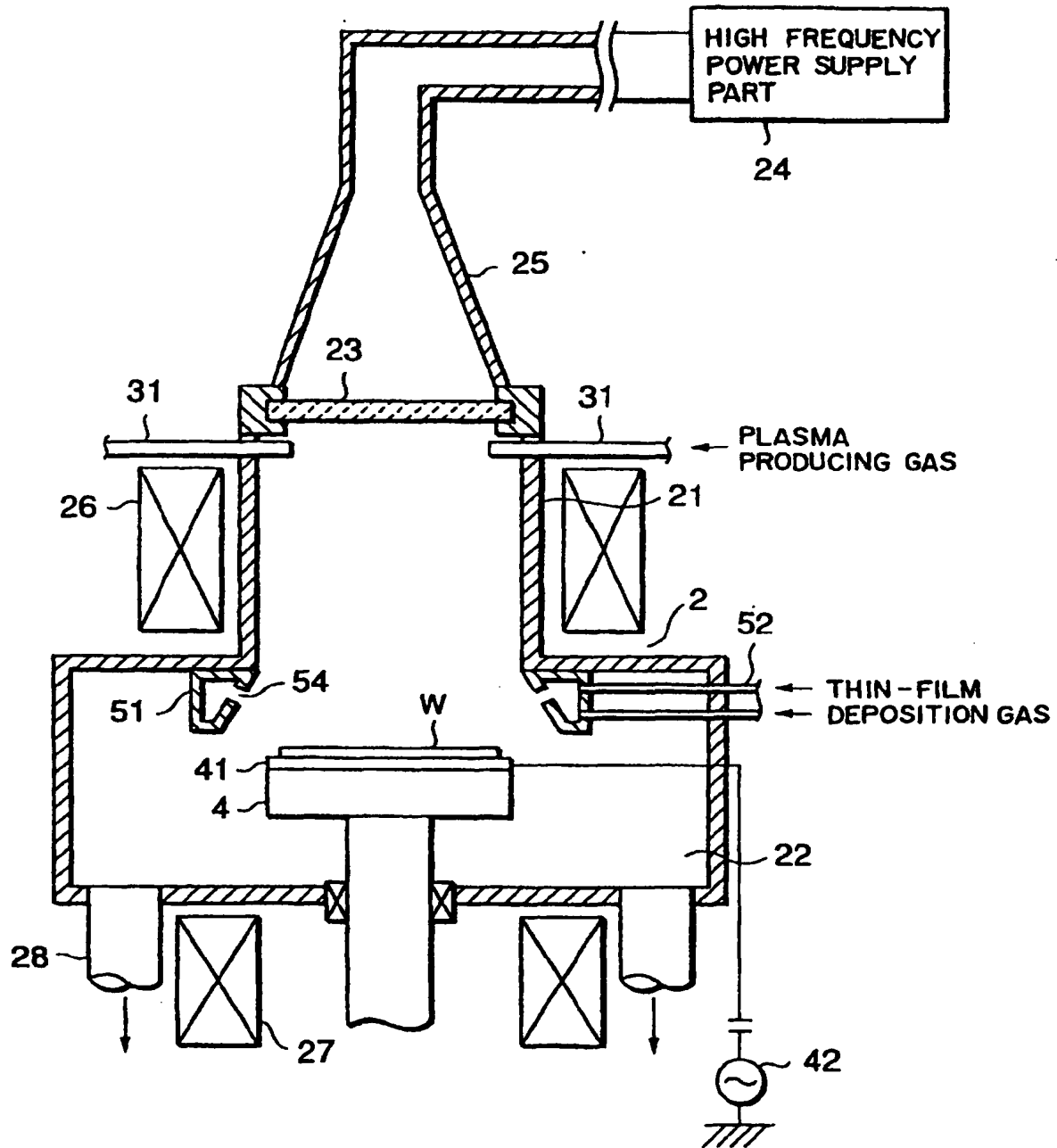


FIG.1

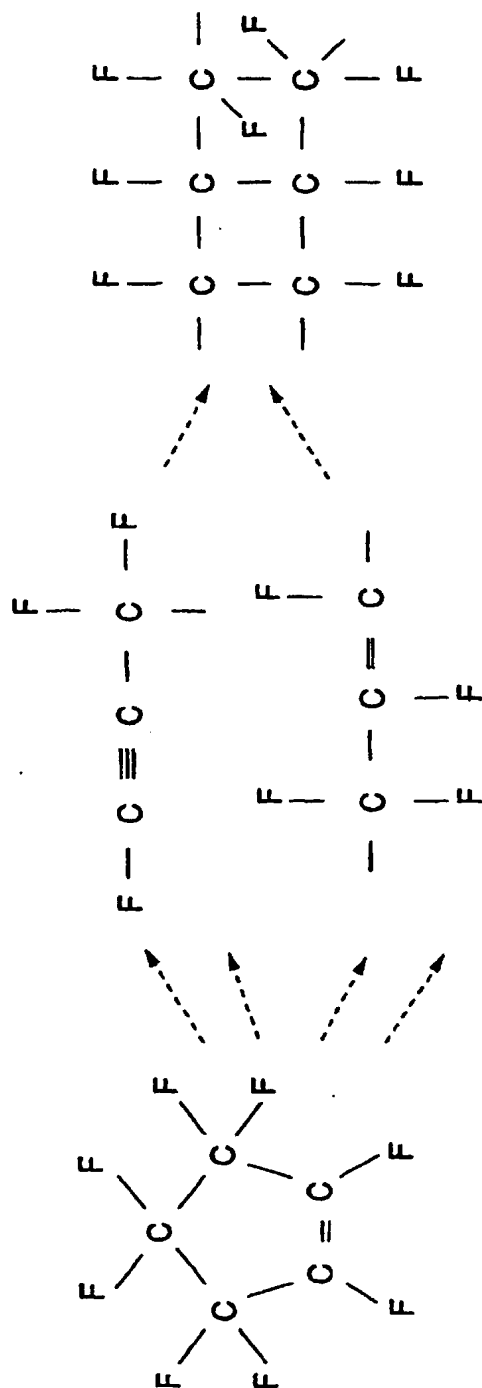


FIG.2

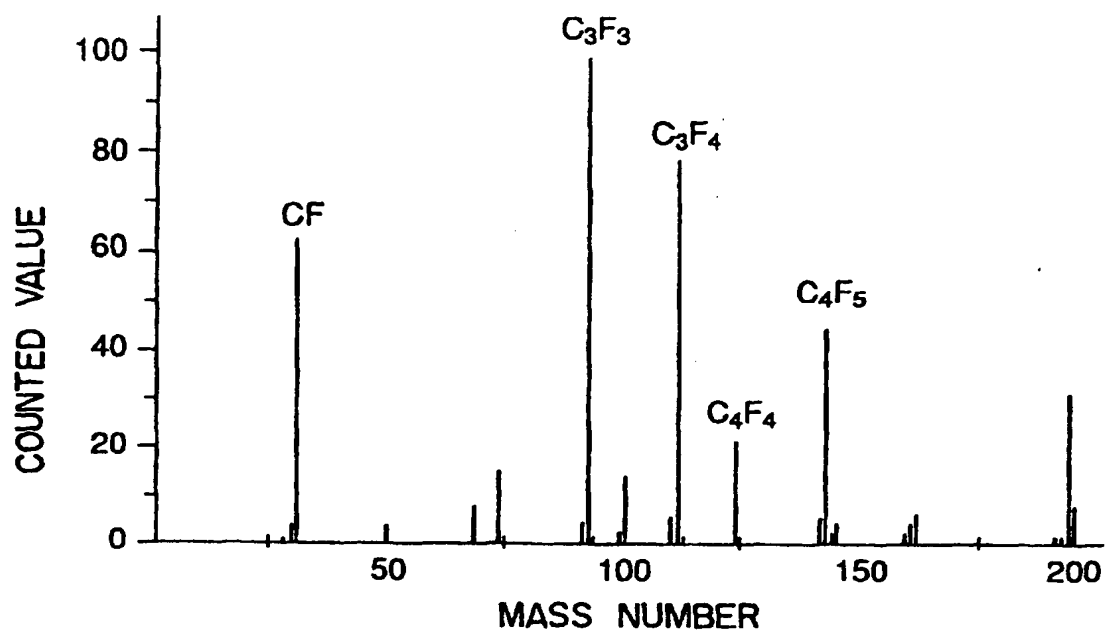


FIG.3

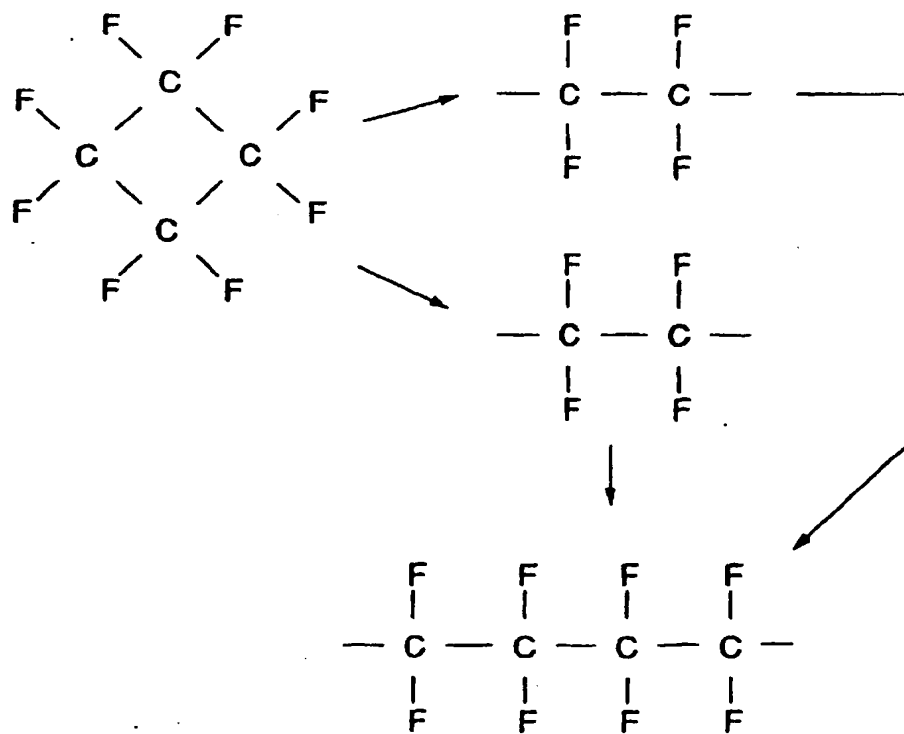


FIG.4

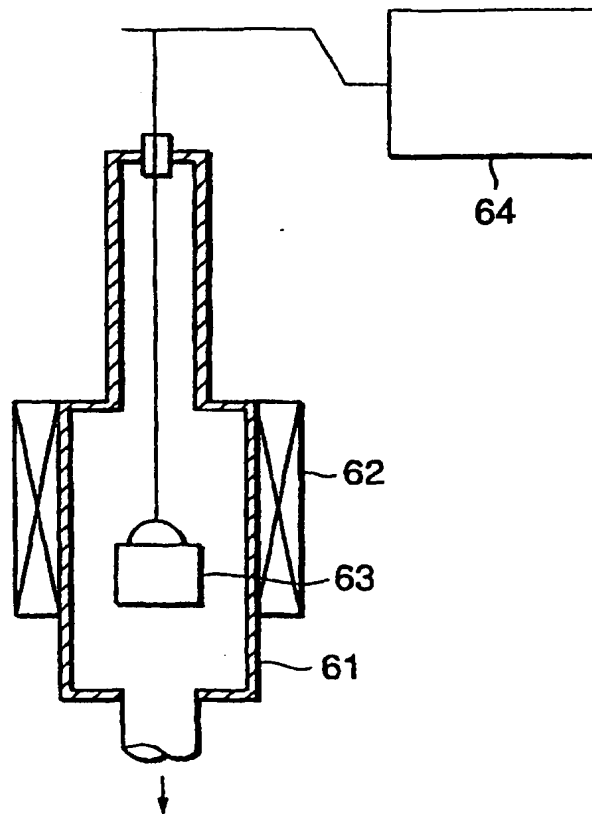


FIG.5

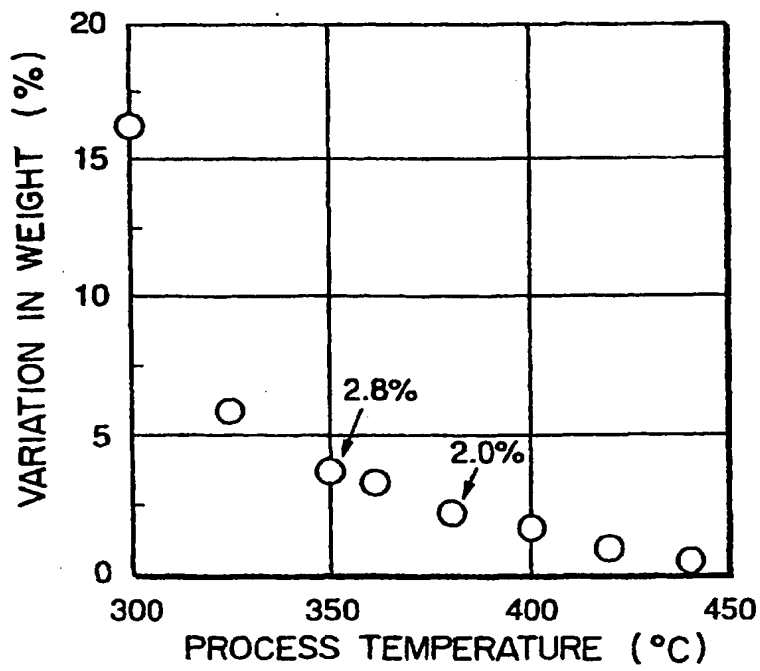


FIG.6

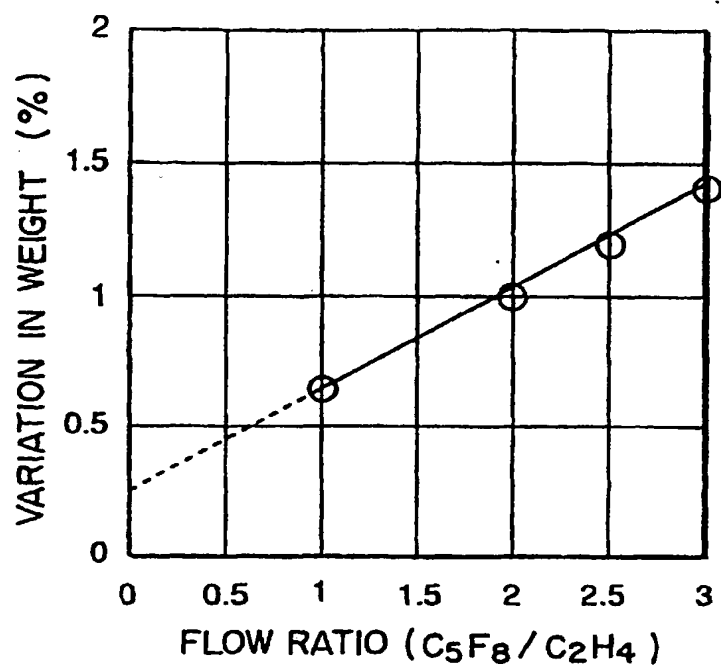


FIG.7

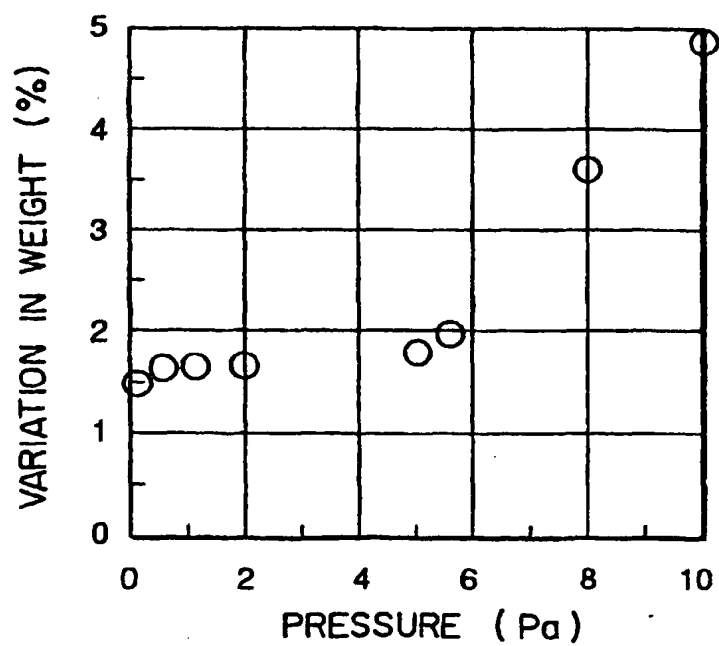


FIG.8

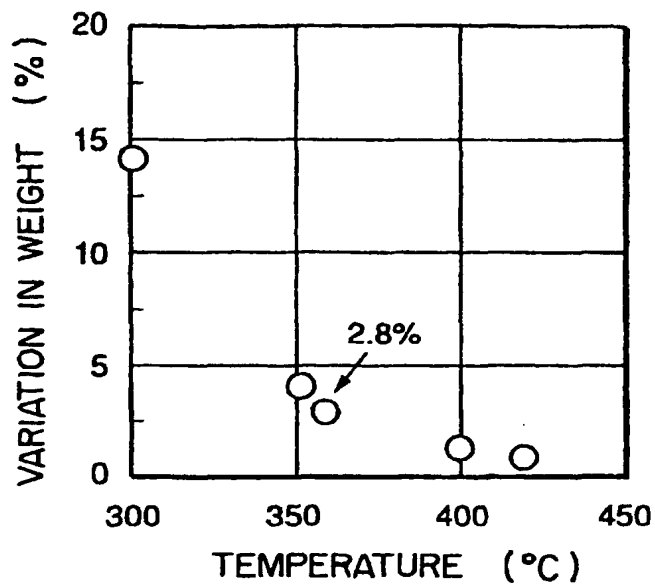


FIG.9

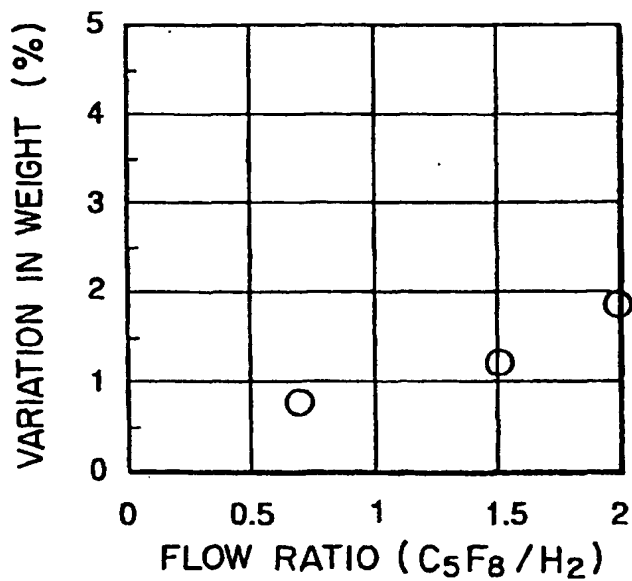


FIG.10

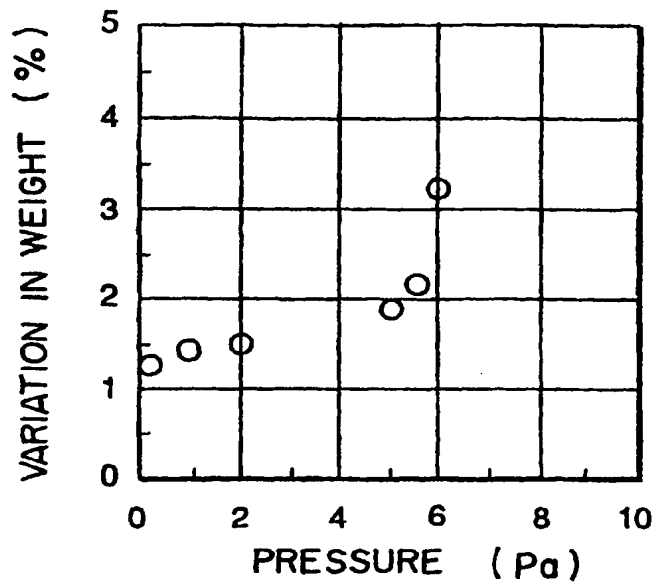


FIG.11

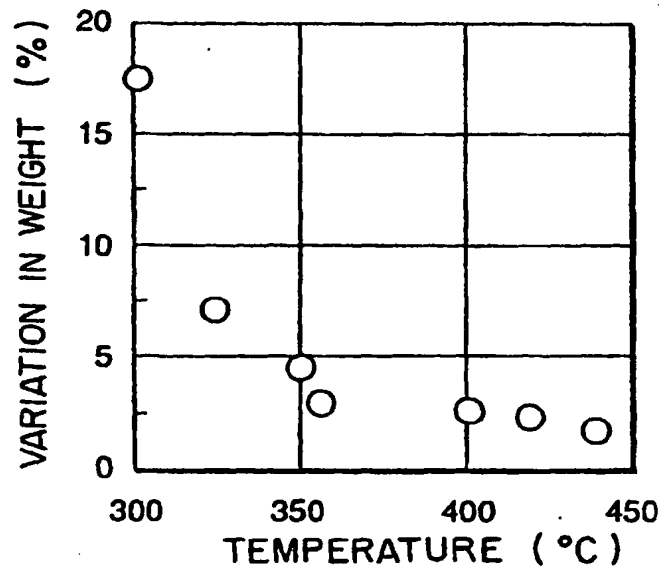


FIG.12

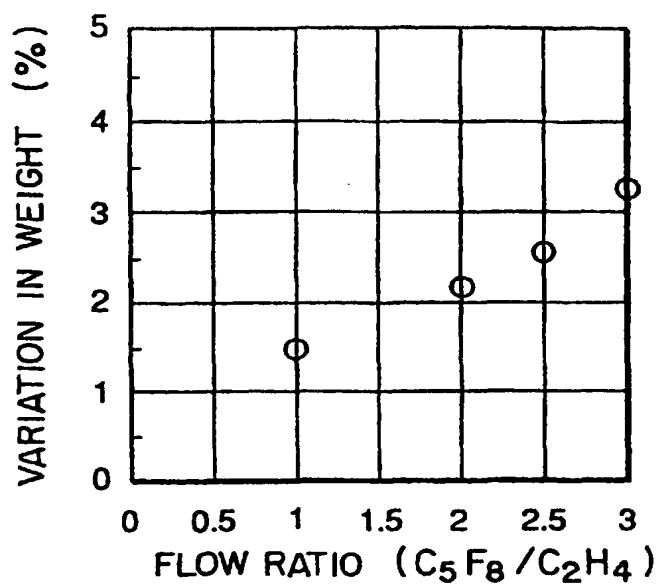


FIG.13

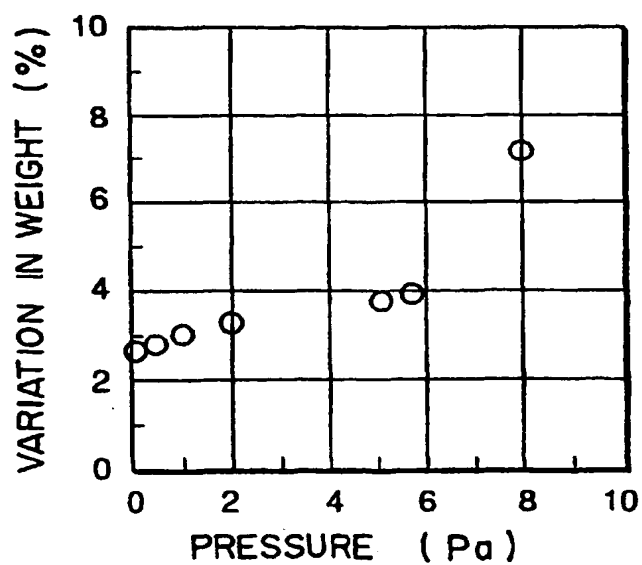


FIG.14

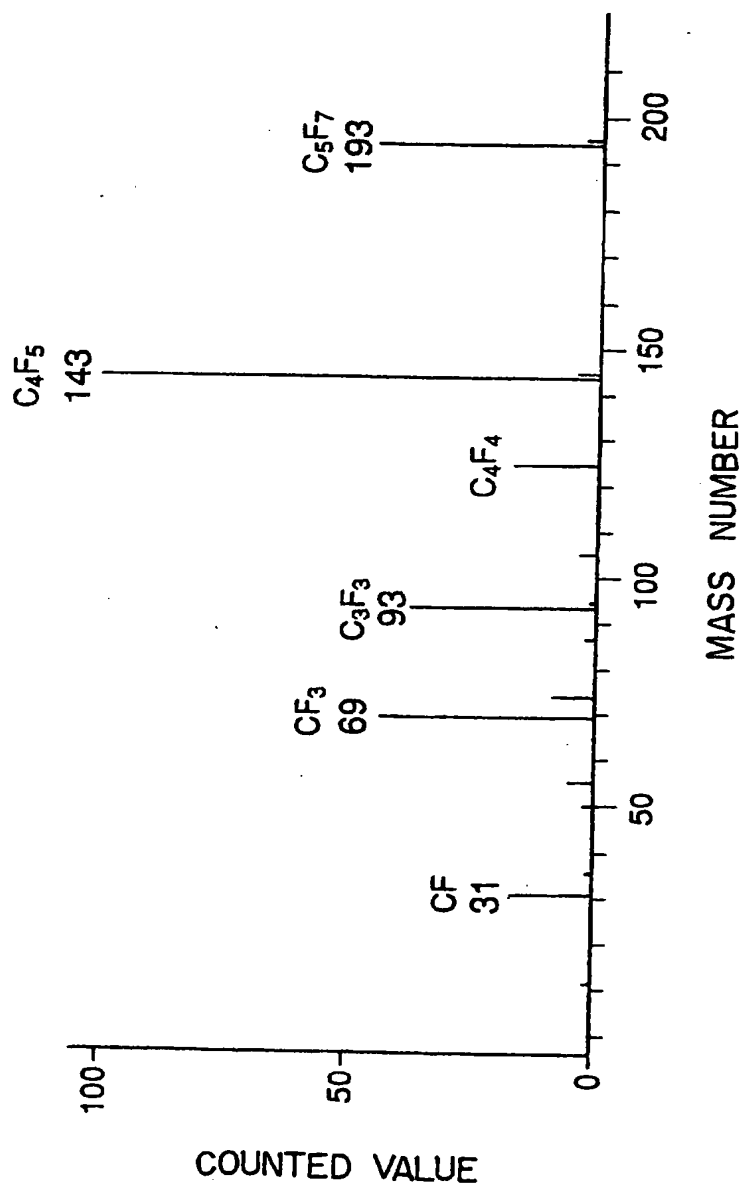


FIG.15

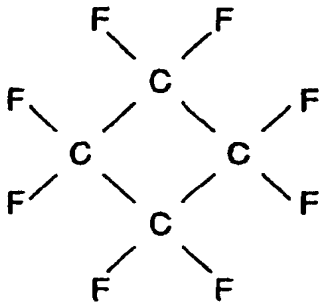
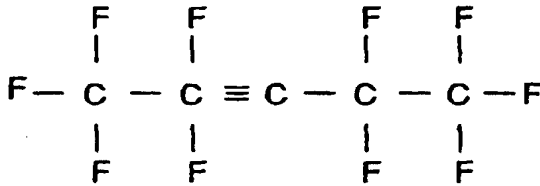
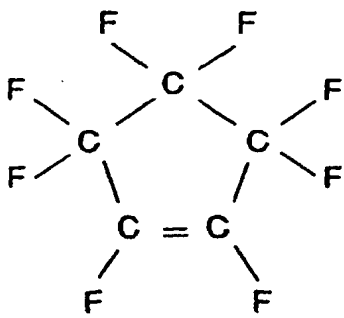
| CHEMICAL FORMULA | STRUCTURE | VARIATION IN WEIGHT (%) |
|------------------|---|-------------------------|
| C_4F_8 |  | 3.7 |
| C_5F_8 |  | 2.6 |
| C_5F_8 |  | 1.4 |

FIG.16

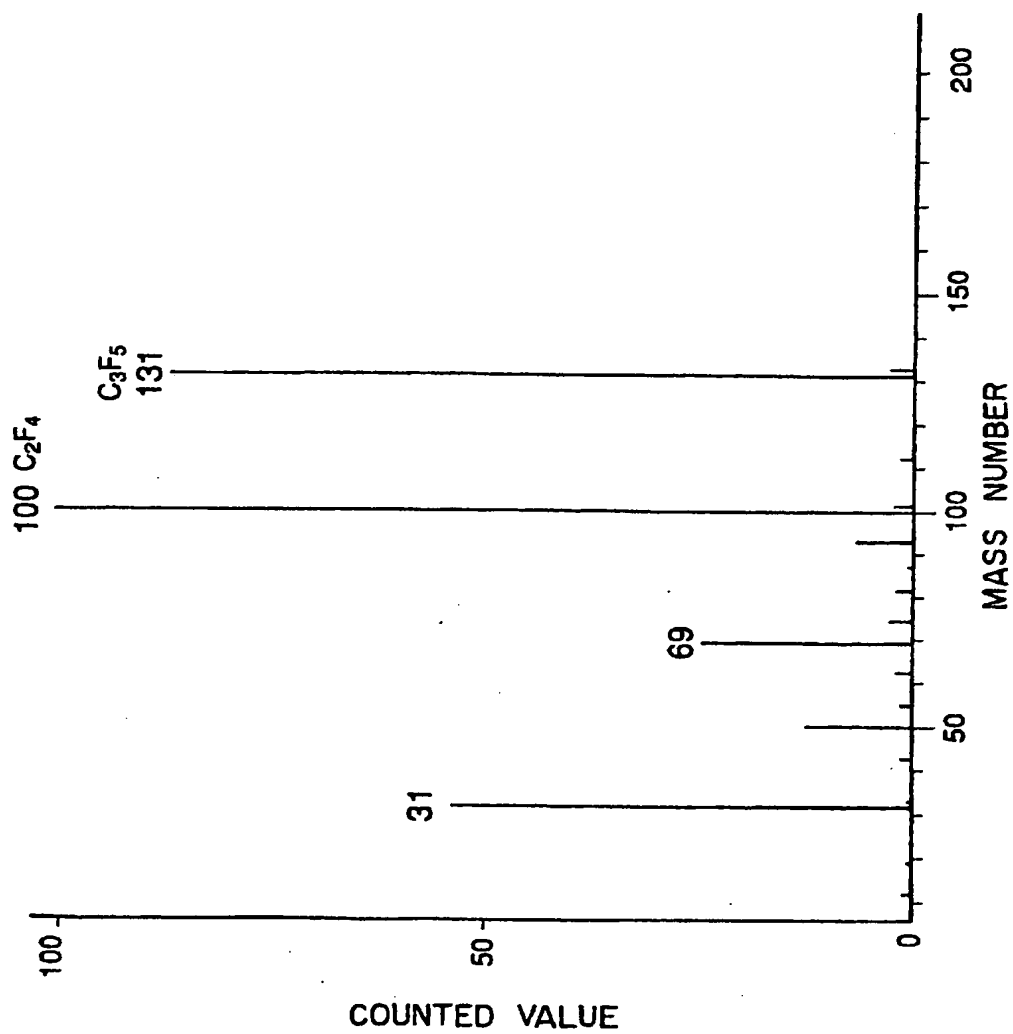


FIG.17

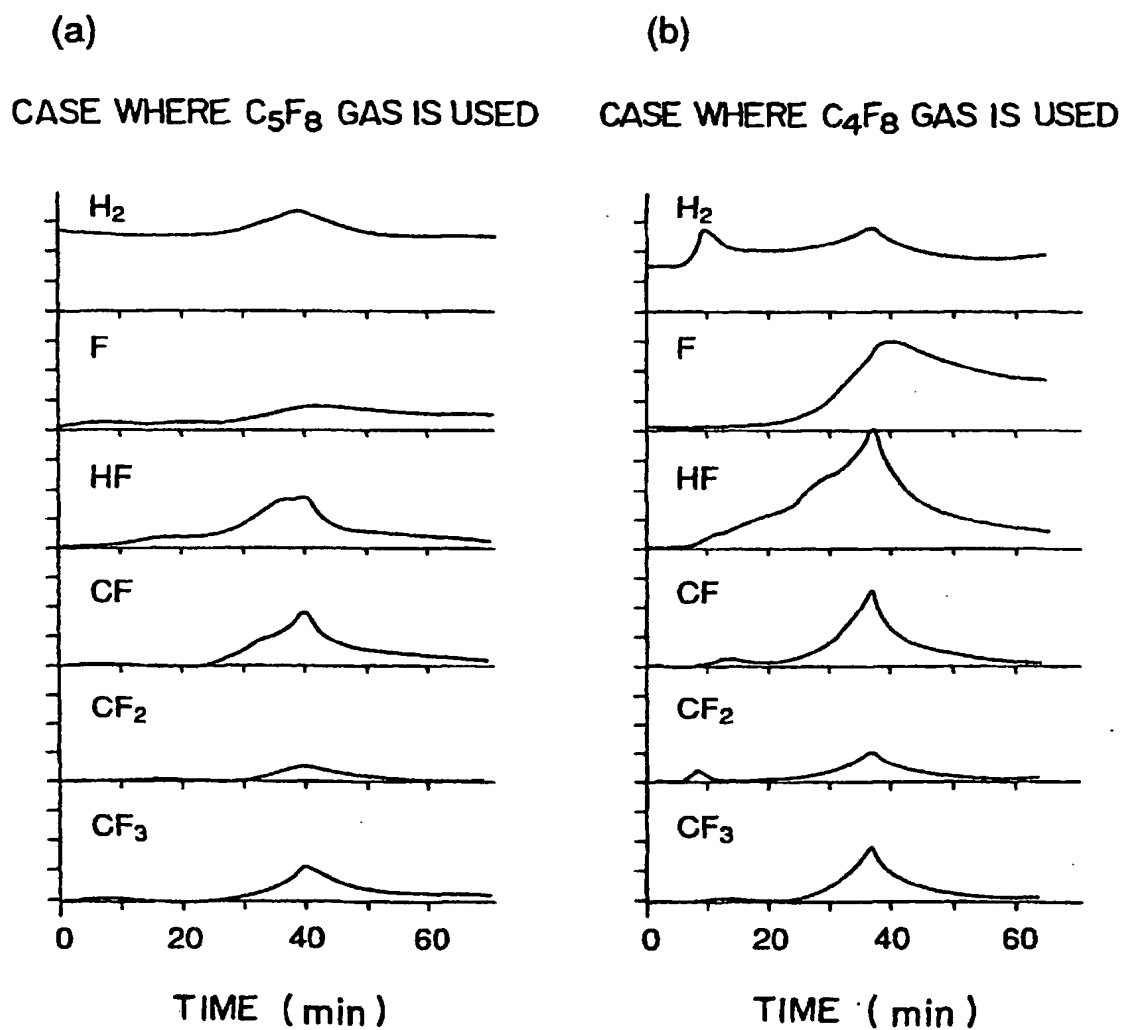


FIG.18

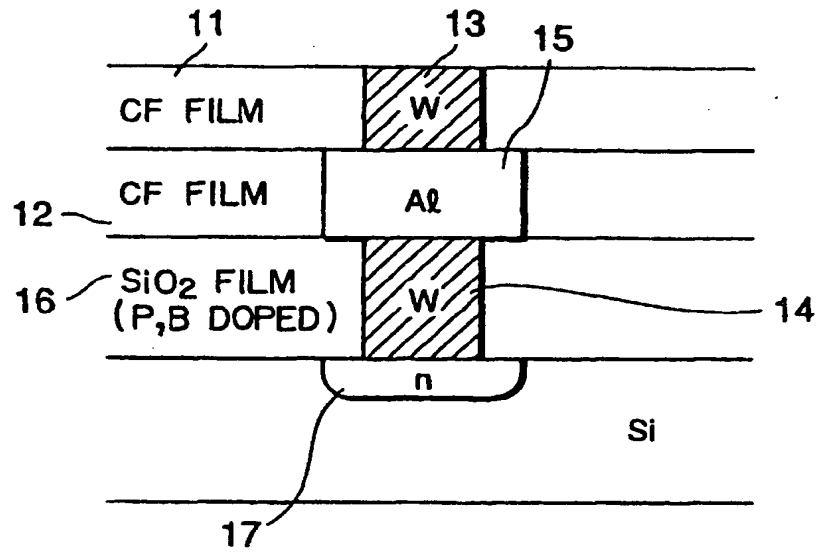


FIG.19

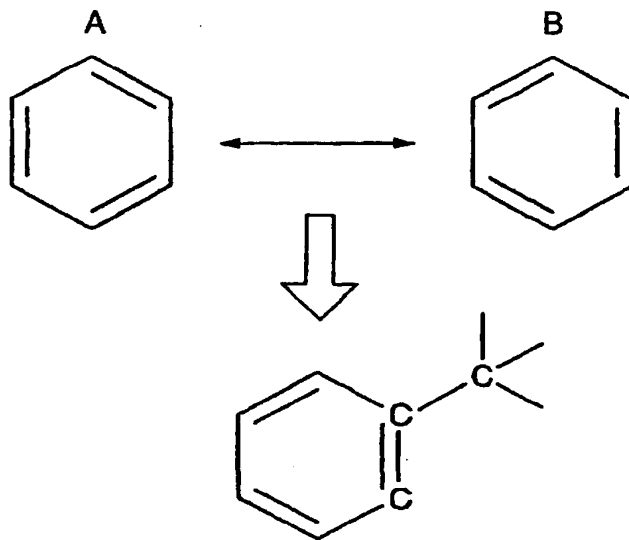


FIG.20

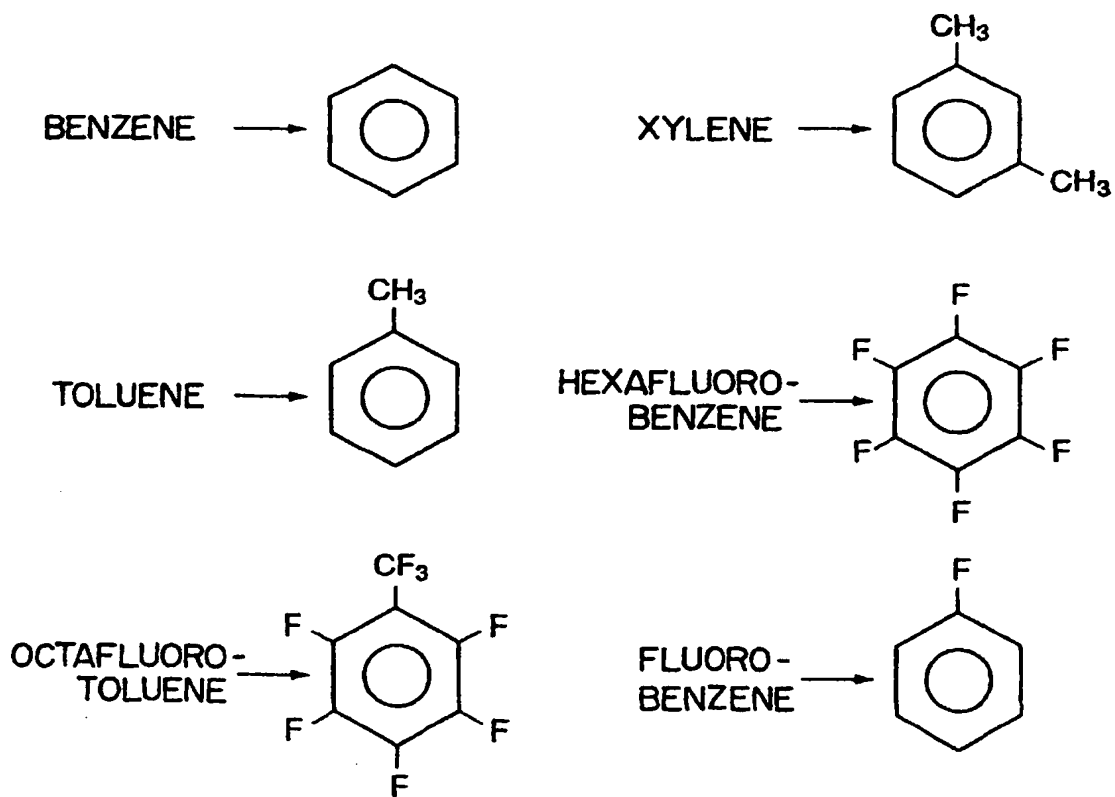


FIG.21

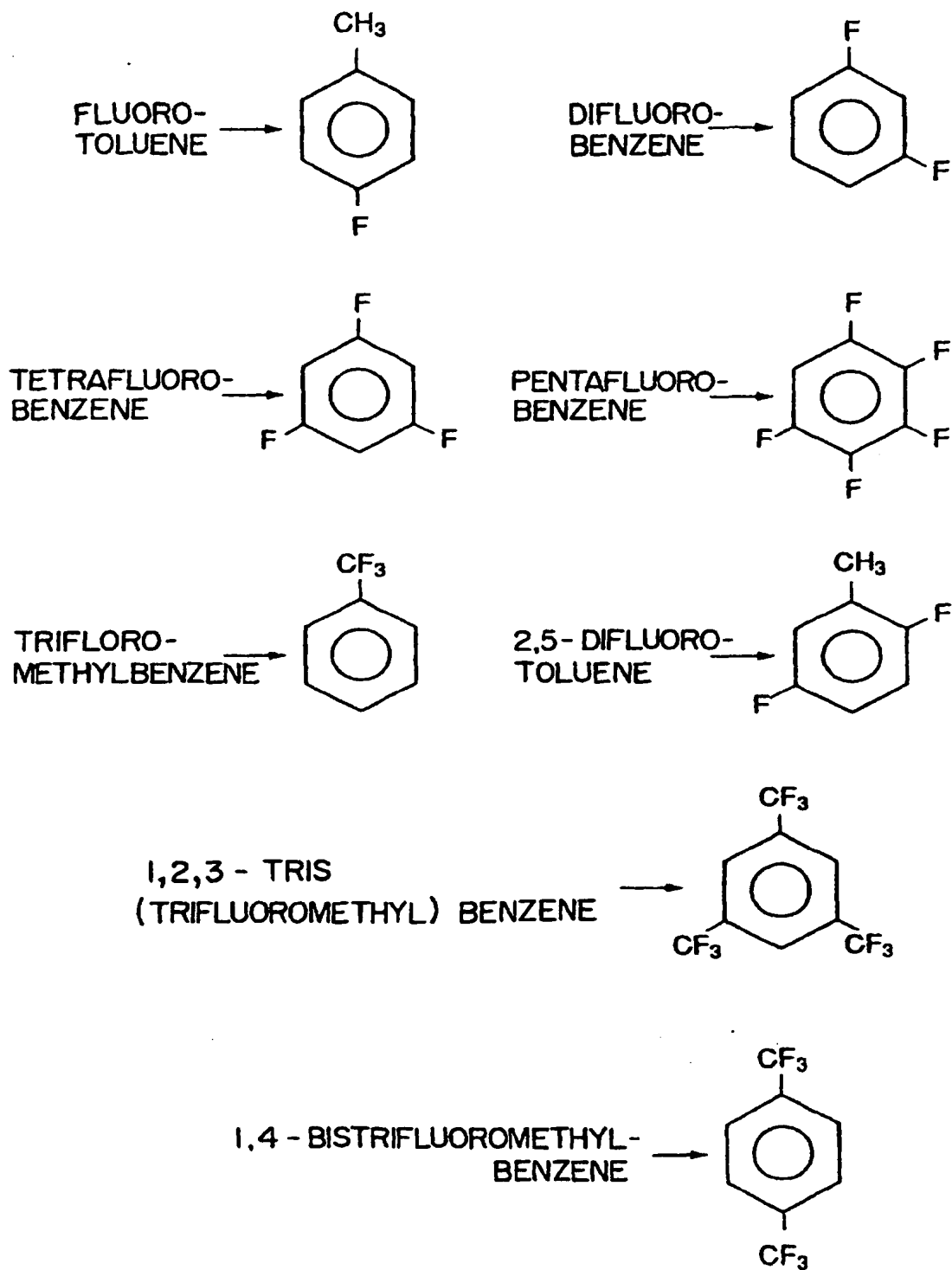


FIG.22

| | THIN - FILM DEPOSITION GAS | MICROWAVE POWER (kW) | BIAS POWER (kW) | VARIATION IN WEIGHT (%) |
|------------------------|---|------------------------------|----------------------|---------------------------------|
| EXAMPLE 1 | C ₆ F ₆ | 1.0 | 0.5 | 1.4 |
| | C ₆ F ₆ | 1.0 | 1.0 | 1.4 |
| | C ₆ F ₆ | 1.0 | 1.5 | 1.5 |
| | C ₆ F ₆ | 0.8 | 1.5 | 1.6 |
| | C ₆ F ₆ | 1.0 | 1.5 | 1.5 |
| | C ₆ F ₆ | 1.5 | 1.5 | 1.2 |
| EXAMPLE 2 | C ₇ F ₈ | 1.0 | 1.0 | 1.9 |
| EXAMPLE 3 | C ₄ F ₈ /C ₇ H ₅ F ₃ | 1.0 | 1.0 | 2.2 |
| EXAMPLE 4 | C ₄ F ₈ /C ₇ H ₈ | 1.0 | 0.75 | 2.8 |
| COMPARATIVE EXAMPLE | C ₄ F ₈ /C ₂ H ₄ | 2.0 | 1.5 | 4.4 |

FIG.23

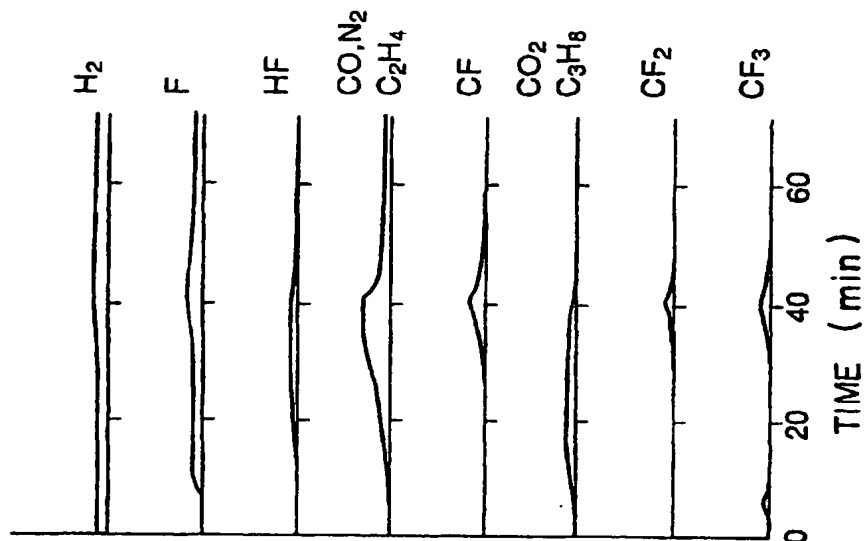
CASE WHERE C_6F_6 / Ar IS USED

FIG. 24

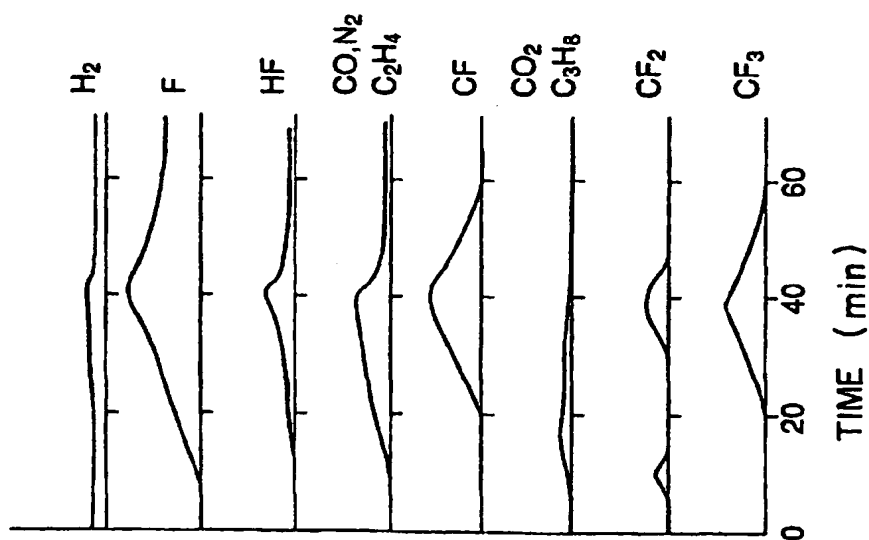
CASE WHERE C_4F_8 / C_2H_4 / Ar IS USED

FIG. 25

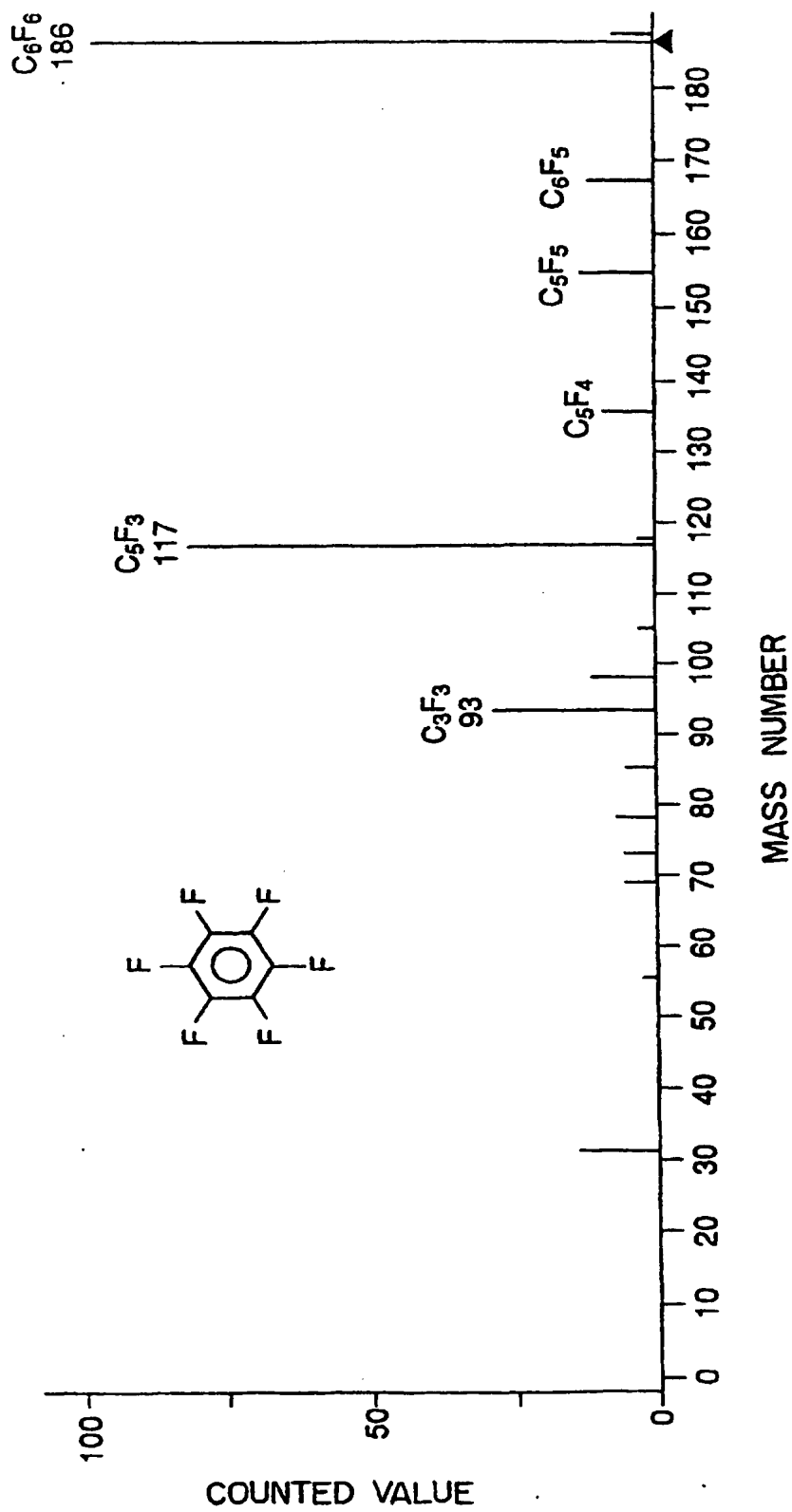


FIG.26

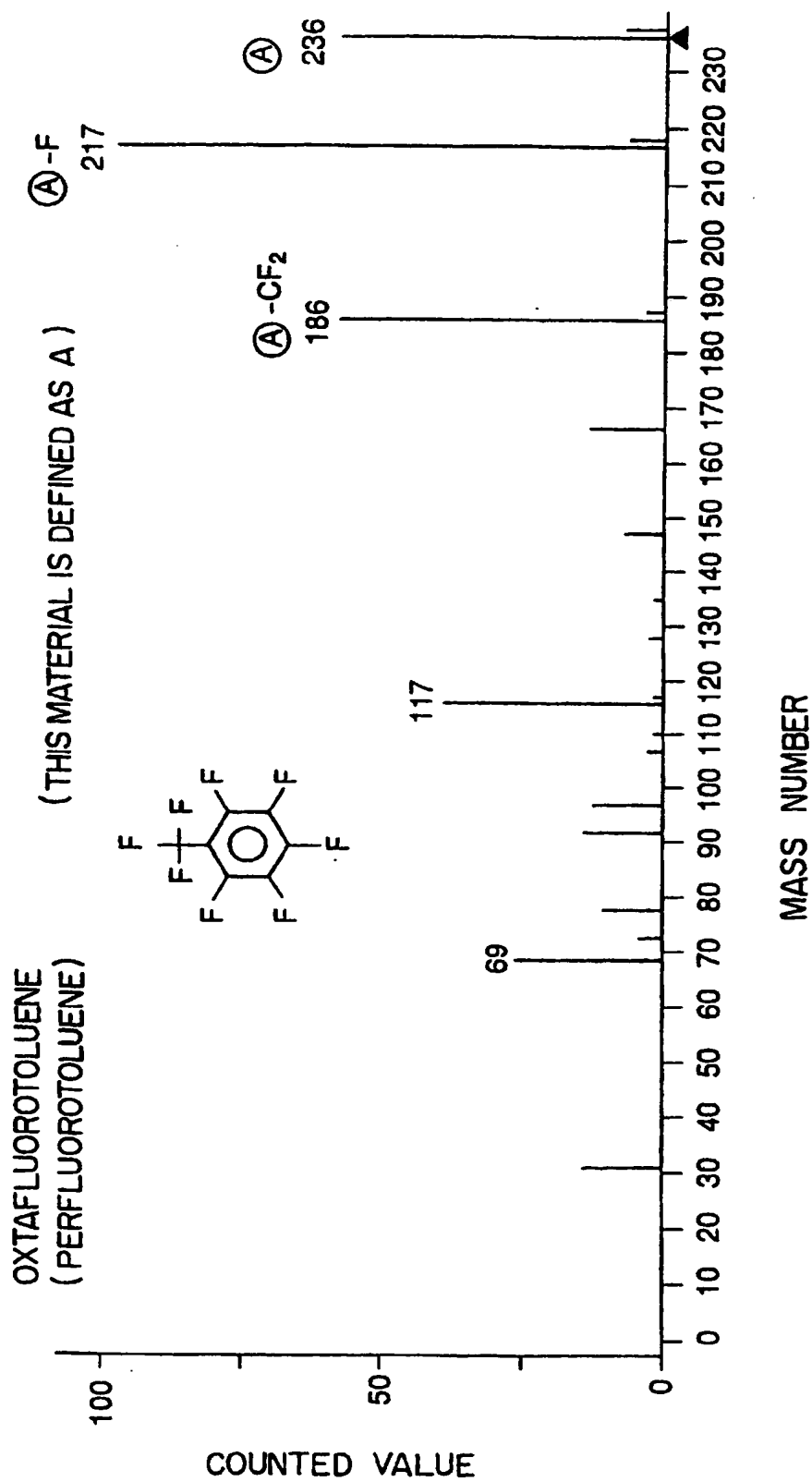


FIG.27

1,4 - BISTRIFLUOROMETHYLBENZENE

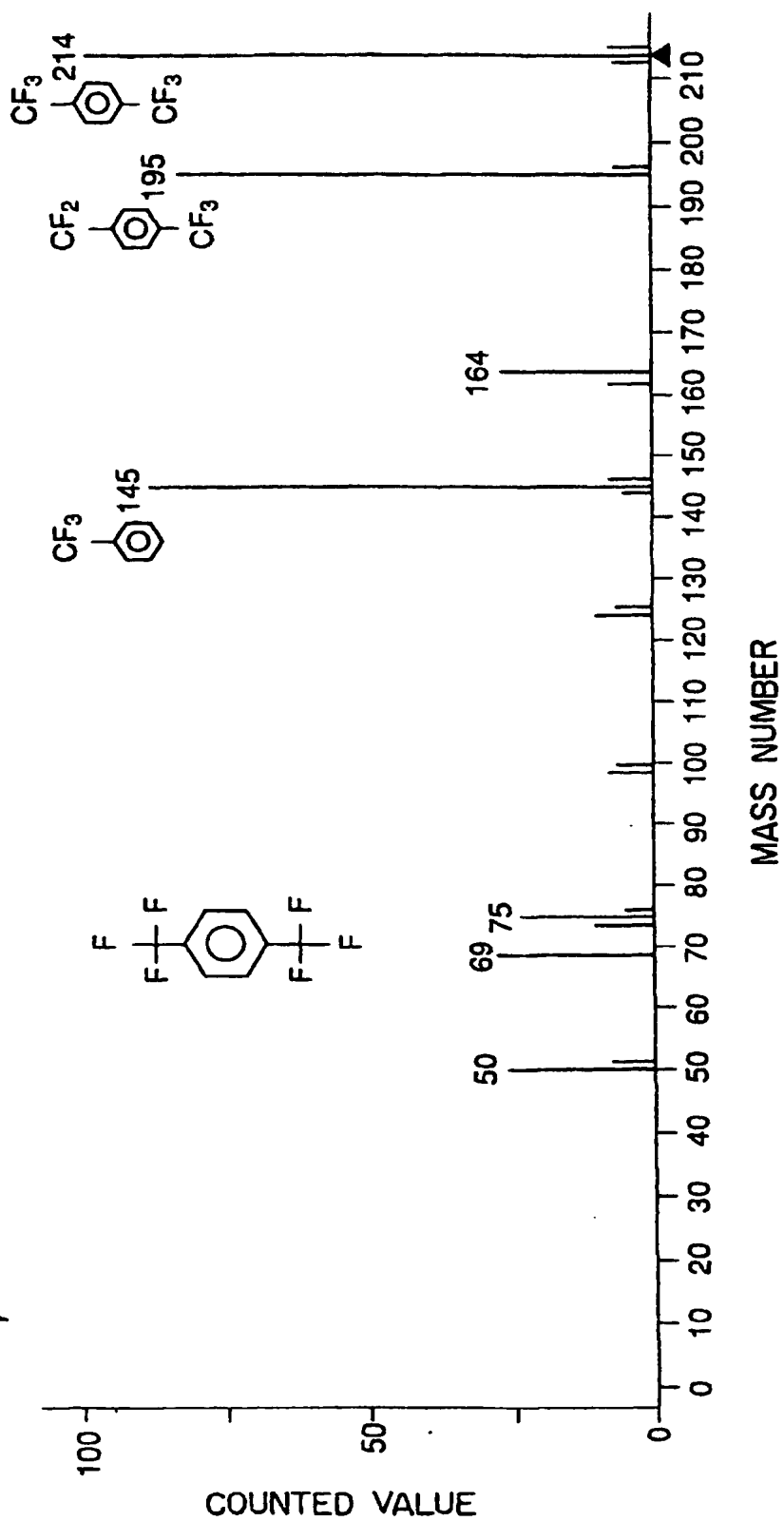


FIG.28

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/05219

| A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁸ H01L21/314 | | |
|---|--|--|
| According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED | | |
| Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁸ H01L21/314, C23C14/00, B01D13/00 | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-1998 Kokai Jitsuyo Shinan Koho 1971-1998 Jitsuyo Shinan Toroku Koho 1996-1998 | | |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | JP, 63-235463, A (Mitsubishi Heavy Industries, Ltd.), | 1, 9-11, 13 |
| Y | 30 September, 1988 (30. 09. 88), Page 3, upper right column, line 8 to lower left column, line 1 (Family: none) | 3, 4 |
| X | Thin Solid Films, Vol. 167, (1988) p. 255-260 | 9, 10, 11, 13 |
| Y | Refer to 2. EXPERIMENTAL DETAILS | 3, 4 |
| A | | 1, 2, 5-8, 12, 14 |
| X | Diamond films and Technology, Vol. 6, No. 1 (1996) p. 13-21 | 9-11, 13 |
| A | Refer to Abstract, 2. Experimental | 1-8, 12, 14 |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex. | | |
| * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family | | |
| Date of the actual completion of the international search 8 February, 1999 (08. 02. 99) | | Date of mailing of the international search report 16 February, 1999 (16. 02. 99) |
| Name and mailing address of the ISA/ Japanese Patent Office | | Authorized officer |
| Facsimile No. | | Telephone No. |

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/05219

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | JP, 9-246263, A (NEC Corp.), 19 September, 1997 (19. 09. 97), Claims 1, 2 ; Par. Nos. [0021] to [0024] & EP, 794569, A & CA, 2199347, A & KR, 97067603, A | 9 |

Form PCT/ISA/210 (continuation of second sheet) (July 1992)